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April 1971

SOLID FUEL-GASEOUS OXYGEN REACTION TECHNIQUES FOR PRODUCING HIGH ALTITUDE BARIUM VAPOR CLOUDS

Space Data Corporation

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Air Force Systems Command
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13. ABSTRACT

Program is to develop superior techniques for producing dense barium vapor clouds at high altitudes using sounding rockets. Several possible vapor production reactions are considered and thermochemical computations are performed comparing achievable efficiencies of yielding free barium at high temperatures. Several prime candidate reactions are evaluated for safety in use and practicality in reactor design. A reactor has been designed for future implementation. Thermochemical computations, ground test results and preliminary flight test observations indicate a large increase in vaporization efficiency over previously used reactions.

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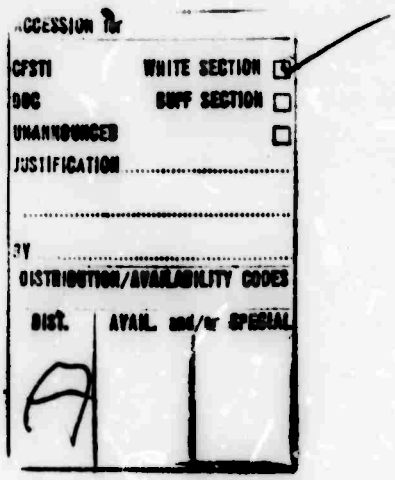

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SOLID FUEL-GASEOUS OXYGEN REACTION TECHNIQUES FOR PRODUCING HIGH ALTITUDE BARIUM VAPOR CLOUDS

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This technical report has been reviewed and is approved.

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FOREWORD

This is a Technical Report covering the period 15 April 1970 to 7 April 1971. This research was supported by the Advanced Research Projects Agency under ARPA Order No. 1057 and was monitored by Rome Air Development Center, Air Force Systems Command, under Contract F30602-71-C-0041.

SUMMARY

A program has been conducted to develop a superior technique far producing dense vapor clouds at high altitudes using saunding rockets.

Several possible vapor production reactions have been cansidered and thermochemical camputatians have been performed ta compare achievable efficiencies af some cambustion reactions yielding free barium at high temperatures. The reactions considered were campared with the n Ba + CuO reaction currently in use for this purpose.

Besides vapor production efficiency, the candidate reactions have alsa been considered from aspects of safety and practicality of reactor design.

Two reactians have been selected:

$$n\,Ba + 1/2\,O_2 \rightarrow BaO + (n-1)Ba \qquad (2)$$

and

$$n\,Ba + Be + 1/2\,O_2 \rightarrow BeO + n\,Ba \rightleftarrows BaO + Be + (n-1)Ba \qquad (3)$$

Thermochemical analyses have been performed on these two reactions to determine the optimum value of n, combustion temperature as a function of n, equilibrium constant for the axygen competition in reactian (3) and vaporization efficiency as a functian of n.

A reactor has been designed to accommodate either of these reactions for ground and flight tests and a light-weight reactor has been designed for implementation of either technique in future Secede operational programs.

Ground tests conducted on both reactions have demonstrated their practicab''ity indicating both reactions to be more energetic than the n Ba + CuO reaction with greater loading af nan-reacted vaparizable barium.

A sub-scale canister cantaining 1 kg af 3Ba + Be + 1/2 O_2 was successfully flight tested indicating greater electron density than given by a 2 kg charge of 1.7 Ba + CuO released fram the same racket [18].

From thermochemical computations, graund test results, and preliminary flight test observations, a 3.5 fald impravement in vaporizatian efficiency has been achieved using the n Ba + 1/2 O_2 system.

A 16 kg release of the 3Ba + 1/2 O_2 is scheduled in November 1971 to further verify this technique.

1. INTRODUCTION

1.1 Program Objectives and Scope of this Report

Under Rame Air Development Center PR Na. A-0-1679, Space Data Corparatian has been warking since 15 April 1970 ta devise and develop a barium vapor deplayment technique having significantly great :r vaparization efficiency than the n Ba + CuO reactian currently in use for Project Secede.

The current scientific abjectives af Project Secede require placement of dense barium ion clouds in the ionasphere. Thus far, sounding rackets have been used to carry chemical payloads with as much as 352 kg of Ba + CuO thermite to the required release altitudes[1].

Estimates of barium vapor yield fram various versions of the n Ba + CuO reaction hove been made and hove ranged between approximately 1% and 10%[2][3][4][5] of the tatal chemical weight which carresponds ta approximately 0.5% to 5% of the achievable gross payload weight assuming a nominal 50% efficiency in payload packaging.

The primary goal of this program has been to develop o vaporizotion technique capable of producing significantly more vapor per paund of payload than has thus for been produced. With increased vaporization efficiency of three, or more smaller payloads and correspondingly smaller and less expensive vehicles will be required ta achieve the SECEDE scientific abjectives.

In addition ta having the capacity far producing greater vaporizatian efficiency, it is necessary that the new technique be capable af implementatian

an a sounding rocket payload at a reasonable cost, and it offer no undue handling hazards.

This report describes same new chemical reactions that seem capable af satisfying these abjectives. Thermochemical analyses, ground test results, and flight test results pertaining ta these reactians are presented. This report reiterates some of the infarmation contained in Interim Report RADC-TR-71-32 dated January 1971. Thermochemical calculations have been significantly refined by using the latest available physical properties data for the chemical constituents[10][11][12][13][14][15].

1.2 Background of Barium Vapor Payload Work

Early work on barium vapor payloads has been summarized in a previaus Project Secede report[6]. In that review, several attempts at producing barium vapor using reduction by aluminum or magnesium or barium peroxide and barium nitrate were cited. Reactions of this type were considered attractive possibilities, since a complete reaction, assuming all the oxygen would react with the magnesium or aluminum, would result in large free barium yields at high temperature. Furthermore, a mixture containing barium in a compound farm (peraxide or nitrate) would be free of the safety hazard presented by the water-sensitivity af raw barium.

Flight tests of these reactions were generally unsuccessful. Apparently, these reactions do not go to the desired completian and BaO, rather than barium vapor, becomes a major reaction product.

The inability of Mg to compete with Ba for O_2 has been further demonstroted by graund tests.

In the n Ba + CuO reaction, which has evolved as the standard technique, the barium itself is the fuel. Thus, there is na question as to what the reoction products will be.

Aside from the present program, recent work has been mostly concerned with the optimizotion of the n Ba + CuO chemistry. An optimum value for n of 2.5 has been selected ond a source of nitrogen in the form of sodium azide, borium azide or sodium nitrate has been added in small quontities to the n Ba + CuO mixture[6][7]. The revision from n = 1.7 to n = 2.5 in this reoction opparently brings about on improvement af obout 17% in vaporizotion efficiency[8]. The oddition of nitrogen is said to bring about more consistent ond improved vaporizotion due to pressure-induced, ropid combustion within the reaction canister ond better particle disintegrotion upon expulsion[9].

Flight tests of "optimized" barium-cupric oxide payloads hove shown little or no improvement in vaporization efficiency compared to the standard 1.7 Ba + CuO reaction[5]. It is apparent that large improvements will require more radicol chonges in the payload chemistry.

Within the last two years several new reoctions have been proposed using barium with very energetic solid oxidizers such as sodium superaxide, sodium nitrote, barium nitrate, lithium nitrate, ond iodine pentoxide[17]. Thermochemicol onolyses of these reoctions predict high yields of the order of two or three times those predicted by similar calculotions on the n Ba + CuO system. Some safety problems have been anticipated in implementing these reactians.

Vaporization of barium using a high explosive as an energy source has also been considered. Theoretical work and some experimental work has been performed[9]. It is estimated by the cited investigators that 30% of the barium compressed by an explosive-induced normal shock wave can be vaporized. This represents approximately 3.5% of the chemical weight. It was estimated that 20% of the chemical energy supplied by the explosive is converted to kinetic energy in the liner and 0.6% into enthalpy of vaporization. The effect of the large kinetic energy on density of the vapor cloud formed is not known.

1.3 The Current Approach to Improved Vaporization

In this program, combustion reactions containing barium and separately packaged liquid or gaseous oxidizers have received major emphasis. Such oxidizers as O_2, Cl_2, F_2, and ClF_3 are very energetic compared to even the best metal oxides and much higher loadings of non-reacting barium can be used to achieve reactions at the same temperatures. The system of reaction products is, in each case, simpler with barium constituting the major component. No other metal is present and the possibilities of the vapor pressure of barium being depressed by solution with another metal or the vaporization process being terminated by higher temperature freezing of another metal are eliminated.

Preliminary thermochemical calculations tabulated in Table I show the halogen systems to have somewhat better mass fractions of non-reacting barium for the same combustion temperatures. Since good high-temperature data on the heat capacities and stabilities of the barium halides are not available,

TABLE 1

THERMODYNAMIC COMPARISONS OF HALOGEN AND OXYGEN REACTIONS WITH BARIUM

Reaction	Combustion Temperature °K	Weight Percentage Non-Reacting Ba
$1.7\ Ba + CuO \rightarrow BaO + Cu + 0.7\ Ba$	3060	31%
$4\ Ba + 1/2\ O_2 \rightarrow BaO + 2\ Ba$	3060	73%
$7\ Ba + Cl_2 \rightarrow BaCl_2 + 6Ba$	3060	80%
$11\ Ba + F_2 \rightarrow BaF_2 + 10\ Ba$	3060	89%
$36\ Ba + 2ClF_3 \rightarrow BaCl_2 + 3BaF_2 + 32\ Ba$	3060	85%

these are very crude calculations. They do indicate, however, gross improvement over the n Ba + CuO system can be achieved using any of these oxidizers. Analyses indicated gaseous oxygen would introduce fewer new problems relative to safety, available reliable thermochemical data; and definition of reaction products than the other candidate oxidizers. Thus, oxygen was selected for primary consideration.

All the reactions in Table 1 show barium used as the fuel. This is a reliable method of ensuring the intended quantity of barium will be released in uncombined form. The idea of using a lighter metal for the fuel component is attractive, however, since the mass fraction of barium in the efflux would be greatly improved. The difficulty of getting magnesium or aluminum to react with oxygen in competition with barium has already been illustrated by the failure of the previously mentioned oxidation reduction reactions. In the current program beryllium, whose oxide has somewhat more negative free energy of formation at high temperatures than those of magnesium, aluminum, or barium, received consideration as a fuel.

To evaluate and compare candidate reactions, thermochemical analyses, ground tests, and flight tests were performed. Analyses predicted the thermodynamic performance of the reaction process under a set of assumed conditions. Ground tests allowed comparison of one system with another and evaluation of parametric variations in a given system under another set of conditions, still not equivalent to those encountered in flight. It is hoped that the combination of analytical and ground test data may be sufficient to predict performance of a

system in a flight test which is, thus far, the only final proof of an improved system.

In this program two reactions:

$$n\,Ba + 1/2\,O_2 \rightarrow BaO + (n-1)Ba$$

and

$$n\,Ba + Be + 1/2\,O_2 \rightarrow BeO + n\,Ba \rightleftharpoons BaO + Be + (n-1)Ba$$

have been evaluated. Analyses and test data on these reactions will now be discussed.

2. THERMOCHEMISTRY

2.1 General

In practical applications of the standard n Ba + CuO reaction, or in either of the new systems under considerotion, combustion occurs very rapidly in on enclosed pressure vessel upon initiation at the desired altitude. High pressure ond high temperoture, resulting from combustion, causes destruction of one or two protective seoling diaphragms; and the reaction products are vented into the ionosphere through small orifices. Up to the point of venting, little vaporization of barium will toke place inside the combustion conister because there is little volume for the vapor to occupy. The majority of vaporization takes place after combustion is complete and during the venting process. Vapor formed by boiling inside the canister will exit os it is formed ond further vaporization will take ploce by boiling from liquid droplets that pass through the exit orifices to the outside.

A method for thermochemicol comparison of these reoctions hos been developed by assuming two sequentiol processes that opproximate the more complex process that seems to take place in flight. The first is adiabatic combustion at constant pressure with only liquid products permitted. The second ideol process is adiabatic vaporization of liquid barium upon release into vacuum.

Since the two ideol processes only approximate the non-ideal real process, the results of these onalyses, expressed in terms of efflux composition, temperature, ond vaporization efficiency, will not precisely correspond to the equivalent real parometers. It is hoped, however, that faults in the analogy will be more or

less equally effective in the three systems under consideration so that comparisons based on the computations will be useful. Ground tests have generally verified the comparisons and flight tests will finally establish the absolute value of vaporization efficiency, the parameter of primary interest.

2.2 Combustion in the Canister

Equations of the three reactions considered are:

$$\underset{137.3n}{\overset{0}{n\,Ba}} + \underset{79.5}{\overset{-37.1}{CuO}} \rightarrow \underset{153.3}{\overset{-132.3}{BaO}} + \underset{63.5}{\overset{0}{Cu}} + \underset{(n-1)137.3}{\overset{0}{(n-1)\,Ba}} \qquad (1)$$

$$\underset{137.3n}{\overset{0}{n\,Ba}} + \underset{16}{\overset{0}{1/2\,O_2}} \rightarrow \underset{153.3}{\overset{-132.3}{BaO}} + \underset{(n-1)137.3}{\overset{0}{(n-1)\,Ba}} \qquad (2)$$

$$\underset{137.3n}{\overset{0}{n\,Ba}} + \underset{9}{\overset{0}{Be}} + \underset{16}{\overset{0}{1/2\,O_2}} \rightarrow \underset{153.3}{\overset{-145.7}{BeO}} + \underset{137.3n}{\overset{0}{n\,Ba}} \rightleftharpoons \underset{153.3}{\overset{-132.3}{BaO}} + \underset{9}{\overset{0}{Be}} + \underset{(n-1)137.3}{\overset{0}{(n-1)\,Ba}} \qquad (3)$$

Above each of the formulas are the standard heats of formation[10][11] in kcal-mole^{-1} and below are the gram formula weights. A good intuitive feeling for the relative thermodynamics of the three reactions can be obtained from inspection of these equations.

First it is evident that the mass fraction of barium in the products increases with increasing values of n. At a given temperature, it is desirable to maximize this quantity.

It should also be evident that, for a given n, a larger mass fraction of barium in the products results from the use of O_2 rather than CuO as an oxidizer. This results simply from the absence of one mole of copper in the products.

The use of beryllium as a fuel can have a very beneficial effect on the output mass fraction. If the equilibrium products of reaction (3) resemble those to

the left of the double arrows, only the 25 grams per mole of BeO contribute to the non-boron fraction. If equilibrium goes to the right, the boron fraction is somewhat worse than in reaction (2) and the beryllium should have been left out.

The energy available to raise the temperature, melt, and vaporize the products is represented by the net enthalpy of formation for each reaction. For reaction (1); $\Delta H_f^\circ = -94.7$ kcal-form^{-1}; for reaction (2), $\Delta H_f^\circ = -132.3$ kcal-form^{-1}; and for reaction (3) $-145.7 > \Delta H_f^\circ > -132.3$. It is evident again, from energy considerations, that O_2 is better than CuO, or for that matter any combined form of oxygen having a negative heat of formation.

Since the heat capacity of a system is roughly proportional to the number of atoms (Dulong-Petit rule), the temperature achieved will be approximately proportional to the negative ratio of the standard reaction enthalpy to the number of atoms in the system. For reaction (1), this ratio is $\frac{95}{n+2}$; for reaction (2), it is $\frac{132.3}{n+1}$; and for reaction (3), it is $\frac{146}{n+2} > X > \frac{132}{n+2}$. Thus, to achieve approximately the same temperature as is obtained in the standard reaction (1) with n = 2.5, we can use, for reaction (2), n = 5.3 and, for reaction (3), 4.9 n 4.3. The non-reactive boron mass fractions corresponding to these values of n are: 49% for reaction (1), 81% for reaction (2), and $96\% > Y > 74\%$ for reaction (3). These values of n and product mass fractions are only approximate because the heat capacities are not uniform and constant and since heats of transition must also be considered. They are, however, remarkably close to those obtained by more precise calculations and they serve to illustrate the effects of a better oxidizer and a lightweight fuel component.

For more precise determination of combustion temperoture for different values of n, it is necessory to solve the equotion:

$$\therefore \Delta H_f^\circ = \int_{298}^{T'} \Sigma C_p \, dT + \Sigma \Delta H_m .$$

where $\Sigma \Delta H_f^\circ$ is the heot of reaction at standard conditions at 298°K; ΣC_p is the total molar heot copacity of the products as a function of temperoture, T' is the temperature ofter all the chemical energy is invested in the products; ond $\Sigma \Delta H_m$ is the summation of molar heats of fusion for all products that fuse below T'.

Since the free energies of formation of both BaO ond BeO hove substontial negative values ot the highest practicol temperotures, it is assumed thot oll of the oxygen is combined with either Ba or Be in ony of the three reactions.

For reaction (3), determination of the product compositions ot equilibrium requires evaluotion of on equilibrium constant for the reoction:

$$(n-1)\,Ba + Be + BaO \rightleftharpoons n\,Ba + BeO$$

If the free energies of formation ($\Delta G_{f_T}^\circ$) are known os functions of temperoture for BaO and BeO, the equilibrium constant for the reaction con be evaluated from

$$\text{Ln } K = -\frac{\Delta G}{RT} \quad \text{where } \Delta G \text{ is}$$

the difference $\Delta G_{f_T}^\circ$ for BaO minus $\Delta G_{f_T}^\circ$ for BeO, ond K is the equilibrium constant. If it is further assumed that the reaction components exist as liquids

in an ideal solution, the concentrations are related to the equilibrium constant by:

$$K = \frac{[BeO]\ [Ba]}{[BaO]\ [Be]}$$ where the

quantities in brackets are mole fractions. To find the values of the four fractions, it is necessary to solve the above equation together with the three equations for conservation of mass. These are:

$$[Ba] + [BaO] = n/(n+1)$$
$$[Be] + [BeO] = 1/(n+1)$$
$$[BeO] + [BaO] = 1/(n+1)$$

It should be noted that K and T are interdependent and that some iteration is necessary to finally arrive at compatible values for temperature and product composition.

The primary thermodynamic data for the elements and compounds of interest are given in Figure 1 and in Table 2. The sources of data are referenced in parentheses in the Figure and Table. The heats of fusion in the table includes the heats of crystalline transitions between the melting point and 298°K. For ΔH and ΔG calculations above 298°, the listed heat capacities were used with linear interpolations between the listed temperature values except where discontinuities occur due to phase transitions.

It should be noted that all of the published data for these substances are not in agreement - especially at the high temperatures. The results to be shown use the data given in Figure 1 and Table 2.

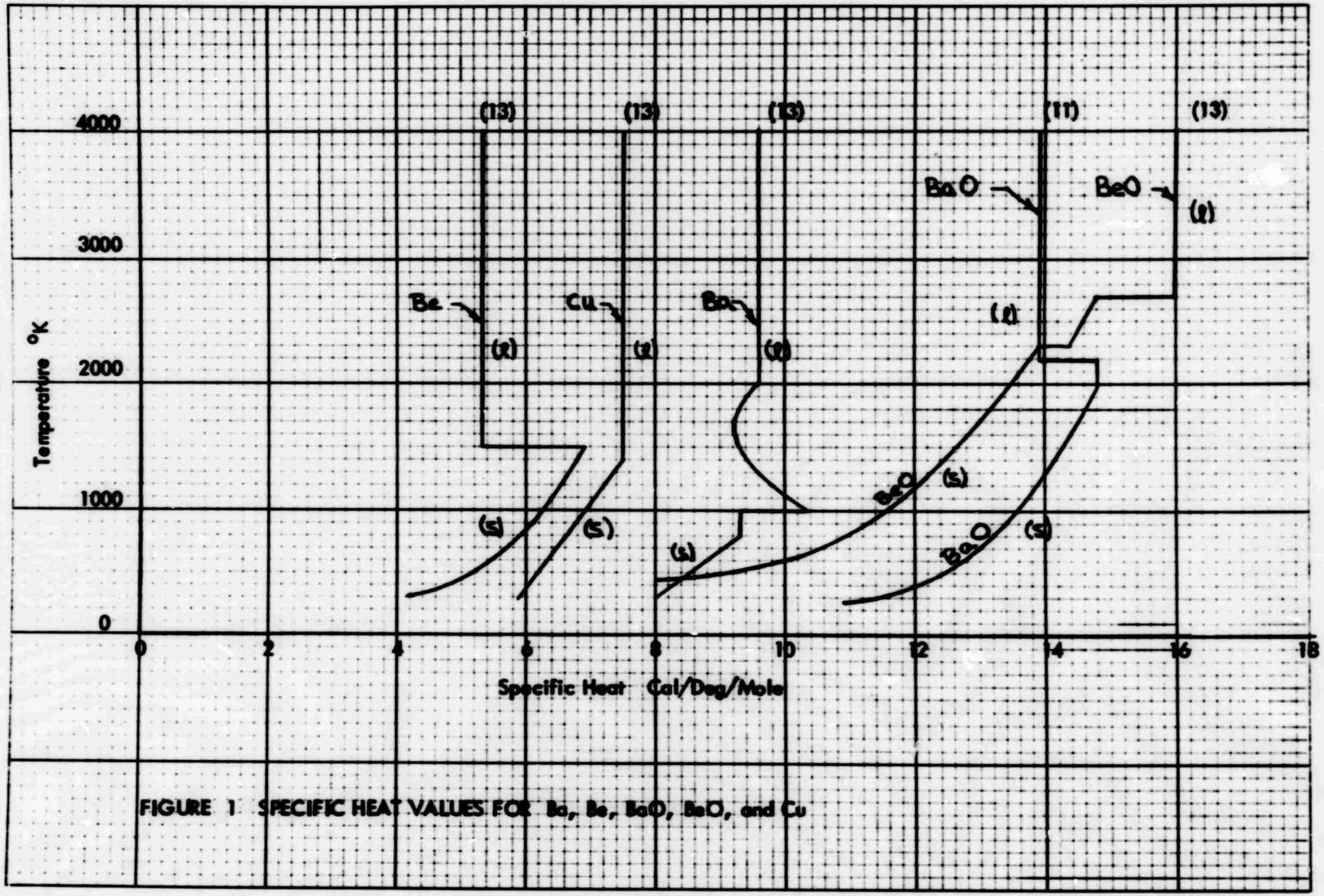


FIGURE 1 SPECIFIC HEAT VALUES FOR Ba, Be, BaO, BeO, and Cu

TABLE 2

THERMODYNAMIC PROPERTIES OF REACTION PRODUCTS

Material	M	ΔH_f°	S°	M. P.	ΔH_m	B. P.	ΔH_v
Ba[13]	137.3	0	15.8	1000	1.9	2122	33.5
O_2	32.0[13]	0	49[13][12]	-	-	-	-
Be	9.0[14]	0	2.3[11]	1556[11]	2.5[13]	3243[14]	
Cu[13]	63.5[13]	0	7.8	1356	3.1	2848	72.7
BaO[11]	153.4[11]	-132.3	16.8	2196[10]	13.8[11]	3000	62[14]
BeO	25.0[13]	-145.7[11]	3.4[11][14]	2707[15]	15.1[13]	-	-

Units: ΔH kcal. mole^{-1}, S° cal. mole^{-1}. $^\circ K^{-1}$, M. P. B. P. $^\circ K$

Symbols: ΔH_f° heat of formation, S° Third law entropy, M. P. Melting Point, M Molecular Weight, B. P. Boiling Point, ΔH_m Heat of Fusion, ΔH_v Heat of Vaporization

Thermochemical results for the in-canister combustion process for all three systems are shown in Figures 2, 3, and 4.

In Figure 2, the fraction of barium in the products is given for varying n. In the n Ba + Be + 1/2 O_2 reaction, the coefficients a, b, c and d are the mole fractions at equilibrium, calculated as previously discussed. For any given value of n, dramatic differences in the barium fraction are not apparent. There is also a temperature difference, however, which will be shown to have a beneficial effect on vapor fraction.

In Figure 3, the dependence on n of reaction temperature is shown for the three reactions. Since the n Ba + 1/2 O_2 reaction produces more heat per atom, it is the hottest for a given n.

In Figure 4, the results plotted in Figures 2 and 3 are combined to illustrate the superior performance of the gaseous oxygen systems. At 3000°K, reaction (2) yields about 74% free barium versus 32% for the reference reaction (1). Reaction (3) yields about 82% free barium at the same temperature.

2.3 Vaporization Upon Release at High Altitudes

Since barium is by far the most volatile of any of the reaction products, and is the major component of reactions (2) and (3), the assumed vaporization model for these two reactions treats the efflux as pure barium.

The incremental temperature change, dx, caused by an incremental conversion of liquid to vapor is given by the equation:

$$dT = \frac{\Delta H_v dx}{C_p (1-X}$$ where

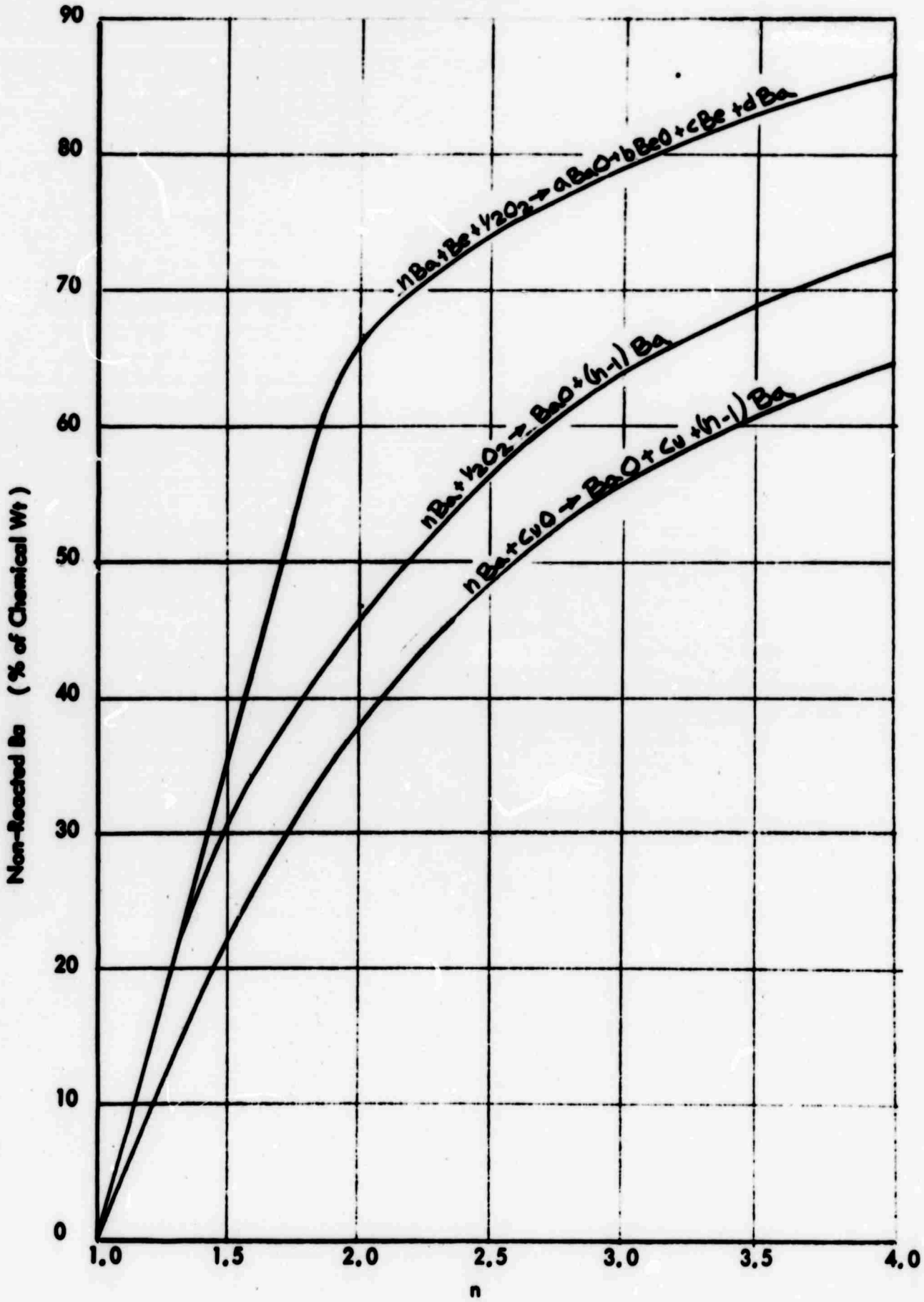


FIGURE 2 NON-REACTED BARIUM VERSUS n

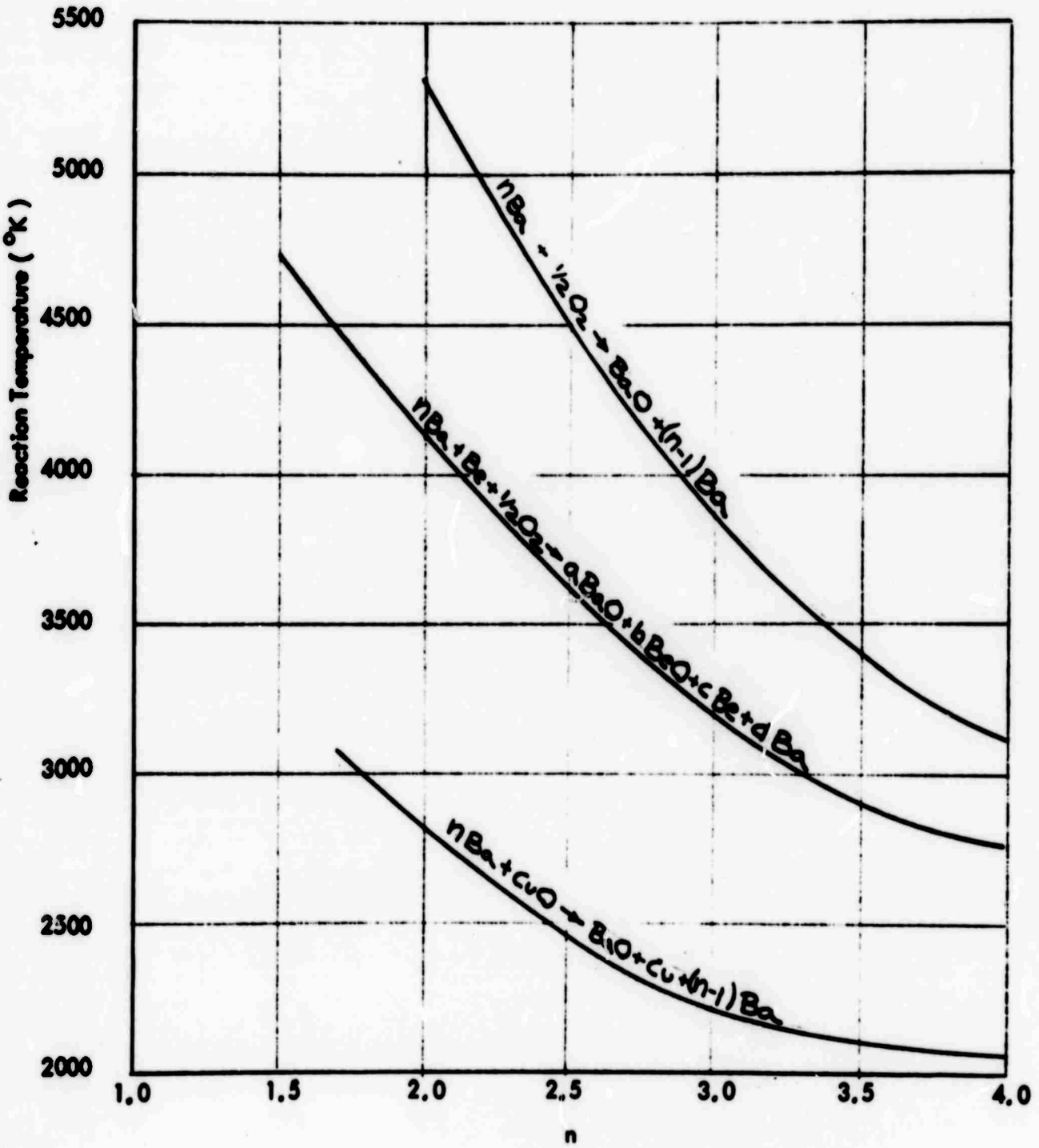


FIGURE 3 REACTION TEMPERATURE VERSUS n

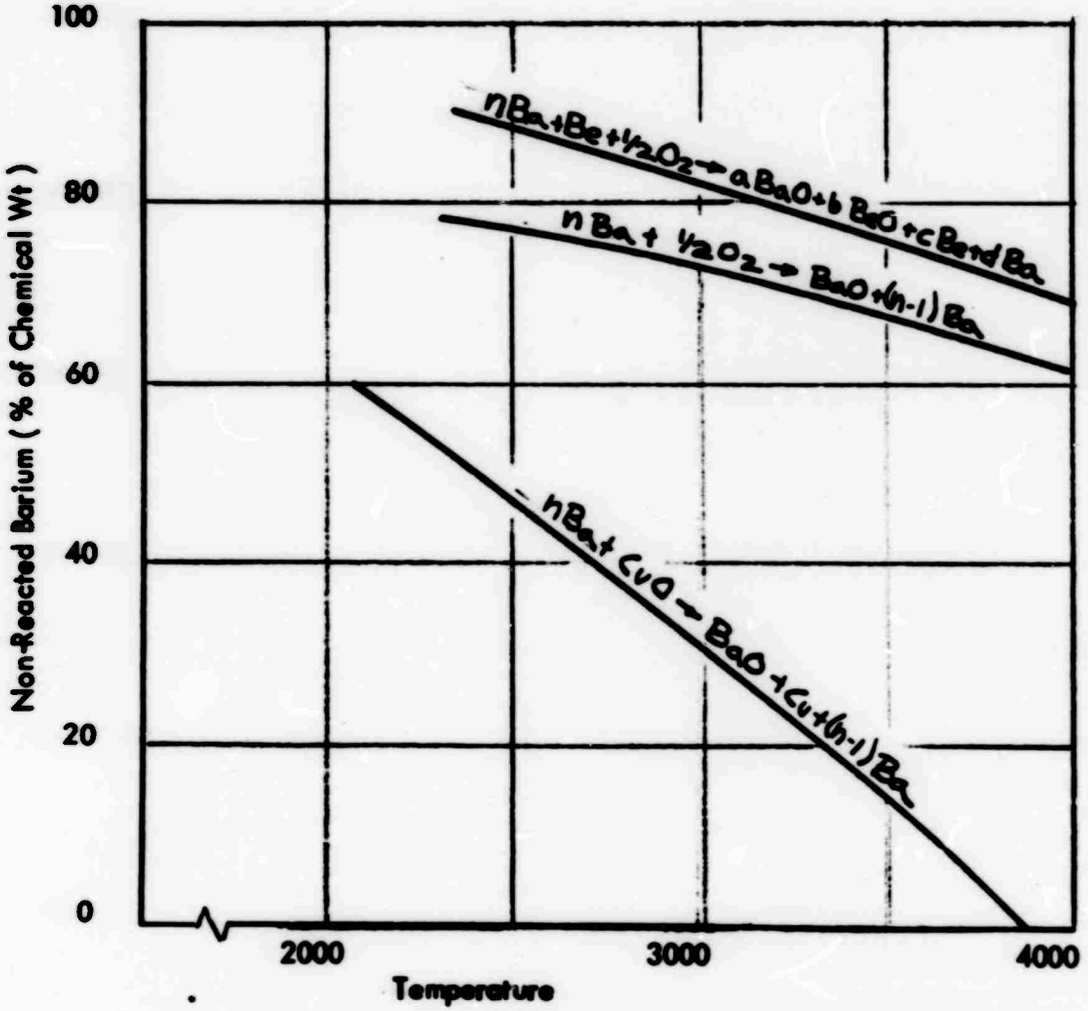


FIGURE 4 NON-REACTED BARIUM VERSUS TEMPERATURE

ΔH_V is the heat of vaporization, dx is the incremental fraction of one mole vaporized, Cp is the heat capacity of the liquid, and x is the fraction vaporized prior to the vaporization of dx.

Integration of this equation from T', the temperature at expulsion, to 1000°K, the freezing point of barium, and using Cp = 9.6 cal. $mole^{-1}.{}^{o}K^{-1}$ and ΔH_V = 33.5 kcal-$mole^{-1}$ gives:

$$T - 1000 = -3489 \ln (1-x)$$

where x is the fraction finally vaporized. This is plotted in Figure 5.

The assumptions in this model are as follows: (a) liquid barium is effectively isolated from the other products; (b) ΔH_V and Cp are constants over the temperature range; (c) no heat is lost to the environment; (d) vaporization begins when the canister is opened and continues until Ba freezes.

For the n Ba + CuO system, reaction (1), the vaporization equation just described is probably much too simple. For practical values of n, Ba constitutes less than half of the reaction products. For each formula weight with n = 1.7 to 2.5, one mole of copper, one mole of BaO, and from 0.7 to 1.5 moles of Ba are present as reaction products. Since copper is another metal, a solution of Ba and Cu is likely to occur with vaporization properties intermediate between those of the two metals. The vapor pressure would thus be depressed and the vaporization process would probably terminate at a temperature closer to the freezing point of copper.

Experimental releases of reaction (1) have been conducted in a vacuum chamber by investigators at the Max Planck-Institution Munich[6][8]. In

Figure 6, these experimental data are plotted along with calculated values for reactions (2) and (3). In these curves, the vaporization efficiency of Figure 5 is combined with the combustion data of Figures 2 and 3.

The peak at n = 2.5 for the standard reaction (1) corresponds to the value now considered "optimum" by most experimenters. For reactions (2) and (3) the best value also appears to be n = 2.5. It should be noted, however, the temperatures at this value of n exceeds 4000°K where thermochemical data is not reliable and where hardware limitations are very severe. n = 3 is considered the least value for reasonably reliable calculations and for practical hardware. At n = 3, the calculated barium vapor fraction for reaction (2) and (3) exceeds the reported experimental value for reaction (1) with n = 2.5 by a factor of approximately 3.8 and 4.0 respectively.

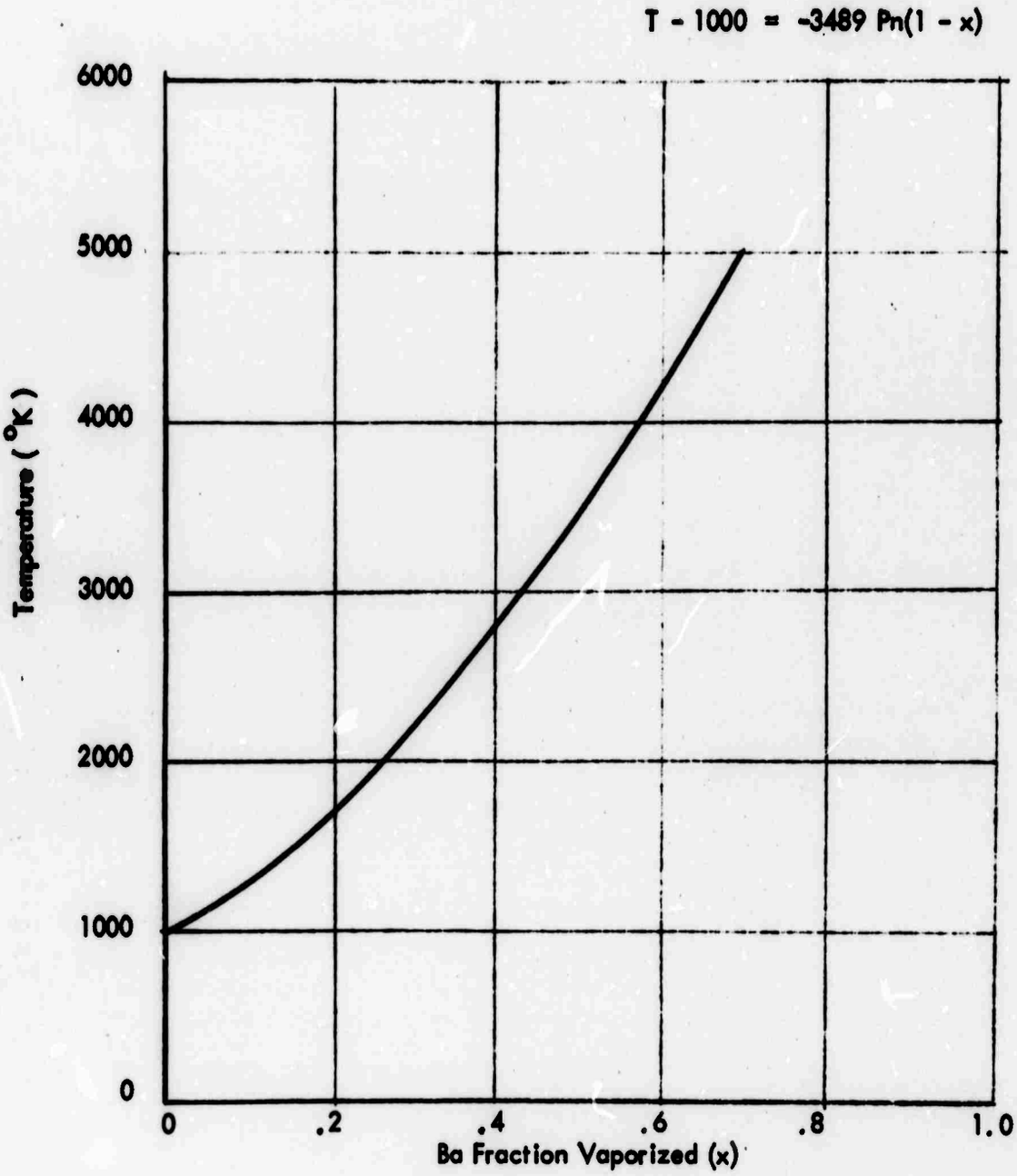


FIGURE 5 BARIUM FRACTION VAPORIZED VERSUS TEMPERATURE

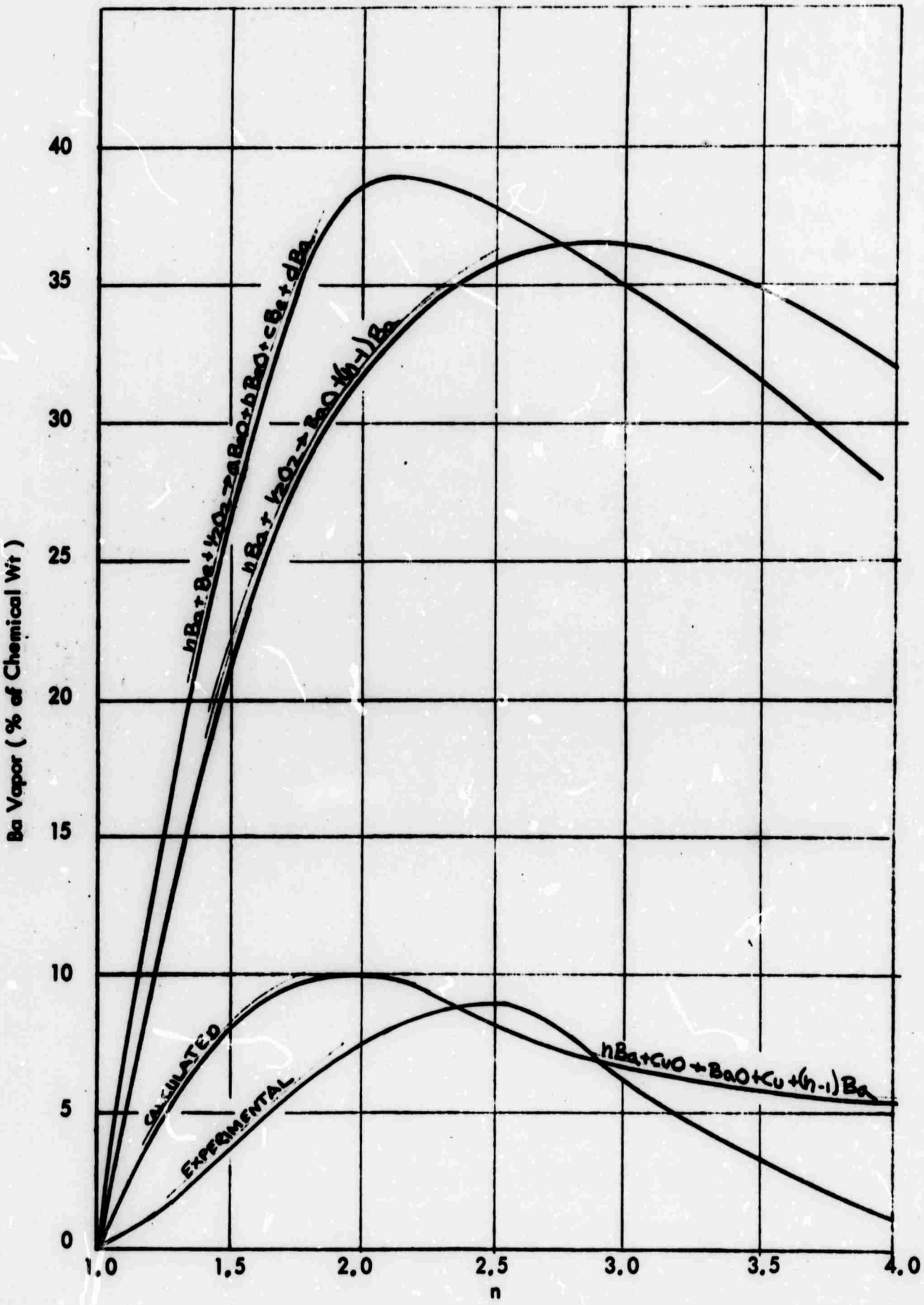


FIGURE 6 WEIGHT PERCENT BARIUM VAPOR VERSUS n

3. COMBUSTION REACTOR DESIGN

3.1 Test Reactor

A boiler plate combustion reactor was designed for laboratory testing as shown in Figure 7. The barium can was 0.960 liters volume whereas two oxygen cylinder volumes were used: 0.470 liters and 0.140 liters.

Three different vent configurations were used, (1) no vents, (2) single vent in the barium base, and (3) dual vent in the barium can cylinder near the base as shown in Figure 7. Vent diameters were 0.5 inches.

To initiate release, the gas generator in the oxygen cylinder is ignited by an electrical ignitor. Gas pressure behind the piston forcibly injects the oxygen through the union containing two protective diaphragms and into the barium can where immediate mixing and spontaneous ignition occurs. The temperature and pressure of the reaction break the protective diaphragms in the barium can and the combustion products are expelled through ports in the can.

The barium reactor was built with sufficient strength to contain the combustion reactions in the closed can configuration.

3.2 Flight Reactor

A light-weight combustion reactor for operational flight use has been devised as shown in Figure 8.

Barium release is initiated by perforating the oxygen tank with cutting charges allowing the chemicals to mix. Spontaneous ignition occurs, the

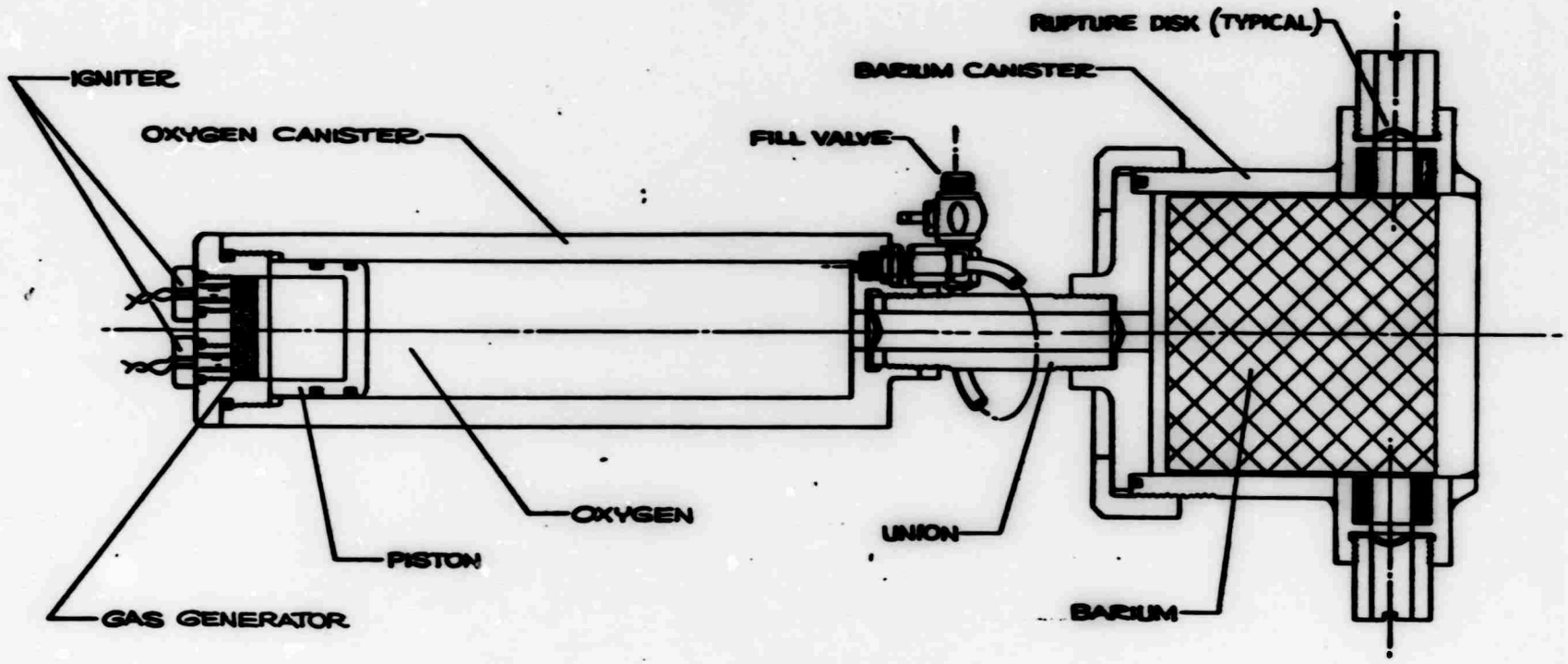


FIGURE 7 GAS - SOLID COMBUSTION REACTOR - TEST

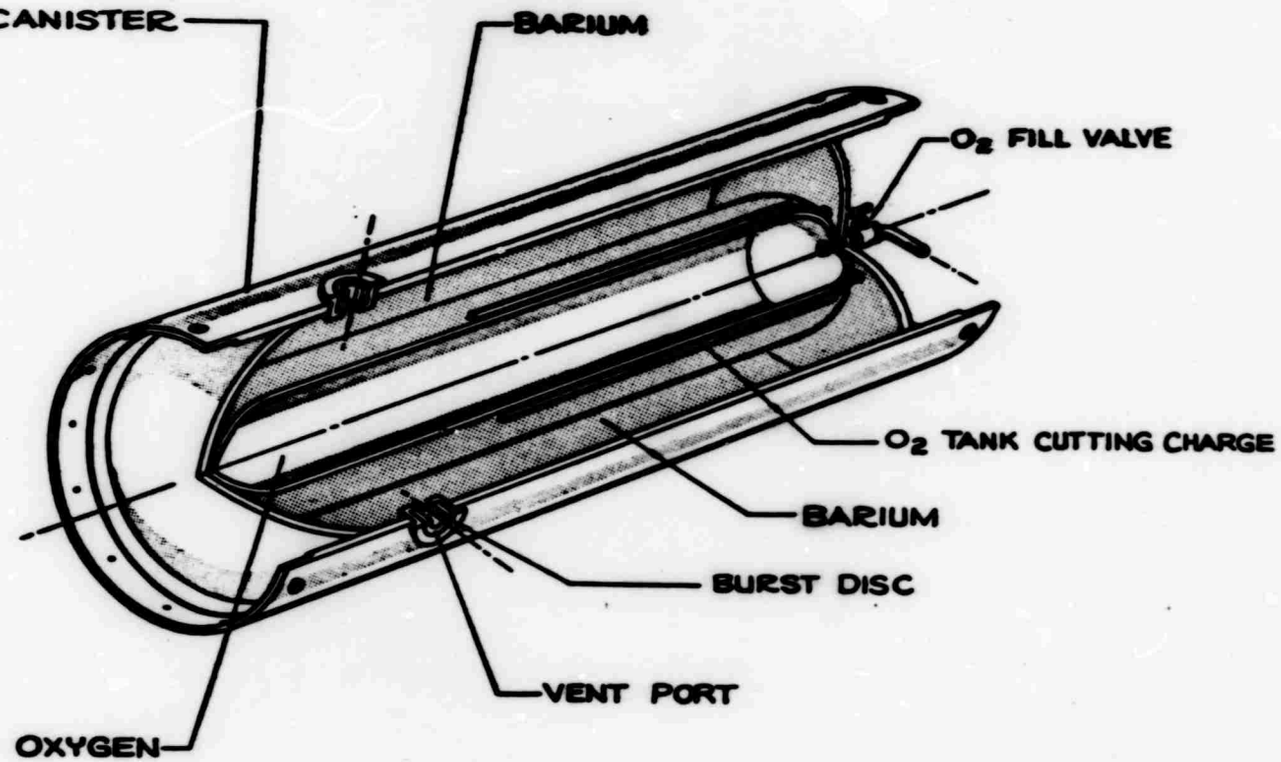


FIGURE 8 BARIUM OXYGEN COMBUSTION REACTOR
(FLIGHT CONFIGURATION)

protective rupture discs are destroyed and the combustion products are expelled through ports in the can.

Preliminary prototype tests of this reactor have been successfully run to verify operability of this design.

A major feature of the gaseous oxygen systems, using either reactor design, is improved safety compared with the barium-copper oxide systems. The oxygen is not loaded until just prior to launch, and the loaded barium canister is shipped and handled as non-explosive material.

4. GROUND TESTS

4.1 General

A series of ground tests were run to determine the combustion properties of the two-phase reaction system.

The test reactor design described in Section 3.1 was used with a non-venting closure and with two venting configurations, one a single vent port, 0.5 inches in diameter, located in the Ba canister base and the other a double vent having two 0.5 inch diameter ports located in the cylinder base as shown in Figure 7.

Combustion tests were instrumented with a pressure transducer and oscillograph recorder to get pressure-time traces. From these traces, the combustion times and the relative temperatures of different reactions and parametric variations in a single reaction were estimated.

On several closed canister tests, analysis of the solid reaction products were obtained by densitometric methods and by measuring the hydrogen evolution obtained when a sample was allowed to fully react with water. In this manner, the relative concentrations of Ba, Be, BaO, and BeO were measured and compared with those determined from equilibrium calculations.

Venting tests were made to determine time and completeness of venting. Analyses were made of the products remaining after completion of venting and the composition of the vented products was thereby estimated.

4.2 Test Results

A summary of ground tests is given in Table 3. Four tests of reaction (2) were made with four different values of n. Two were venting tests and two were

TABLE 3 - GROUND TEST SUMMARY

Test No.	Reaction	Configuration SDC PN 428-10	Chemical Wt. (gm)	Temperature Predicted (°K)	Pressure Predicted (psi)	Peak Pressure Measured (psi)	Remarks
6.24.70-1	1.45 Ba + .5 O_2	Single Vent	981	6000+	-	-	Spontaneous ignition Upon O_2 mixing
6.25.70-1	5.85 Ba +.5 O_2	Closed	1973	2570	875	795	Verified Thermochemical Calculations
7.21.70-1	5 Ba + .5 O_2	Closed	843	2920	603	556	Verified Thermochemical Calculations
7.21.70-2	4 Ba + Be + .5O_2	Closed	787	3140	750	1360	Residue % by wt. 79.2% Ba, 18.3% BaO 1.4% BeO, 1.1% Be
7.23.70-1	3.2 Ba + .5 O_2	Single Vent	1944	4130		3420	Bright yellow flame - No burning particles
8.20.70-1	BaO_2 + 2Be	Closed	748	3400	880	440	Low Pressure Indicates Reaction Partially Complete
9.30.70-1	2.7 Ba + Be + .5O_2	Dual Vent	1815	4000		3000	Incomplete O_2 Mixing Reduce Ba loading density for next test.
10.12.70-1	3Ba + Be + .5 O_2	Single Vent	1059	3750		1400	Complete O_2 Mixing

closed canister tests. Three tests af reactian (3) were made, two of which were vented. The sixth test was an attempt at an axidatian-reduction reaction using BaO_2 and Bc.

Pressure was not measured in the first test. Upon injection of O_2, spontaneous ignition occurred. The products were vented in a spectacular fireball resembling thase obtained in similar sized tests af reactian (1) except that it was much brighter (less red) ond the block smake that results from copper oxidation in the atmosphere was absent.

Pressure traces for tests 6.25.70-1 and 7.21.70-1 ore given in Figures 9 and 10. It is observed that the expected combustion temperature for the second of these two tests was higher than for the first but that the peak pressure was higher for the first. If the pressures of these tests ore compared on the basis of ideal gas law applied to o quontity of volatile material, (probably hydrogen from the pentane cleaning agent adsorbed on the surface of the Ba granules) proportionol to the quantity of Ba, the predicted pressures shown in the sixth column are obtained. Since less material was used in the second test, moro canister volume was ovailable for exponsion of this gas ond o lower pressure thus resulted. Predicted pressures based on this technique have been compared against observed pressures in over 20 past tests of the barium cupric oxide system with excellent correlation.

The rise time of both pressure traces is very fast indicating that the reaction takes ploce in less than 10 milliseconds. This adds some confidence to the odiabatic combustion assumption used in thermochemical computations because little heat can be lost by radiation and canduction in such a short time. In past tests af reaction (1) rise times ranging fram 10 to 100 millisecands have been observed.[15] This indicates somewhat slawer combustion for that system.

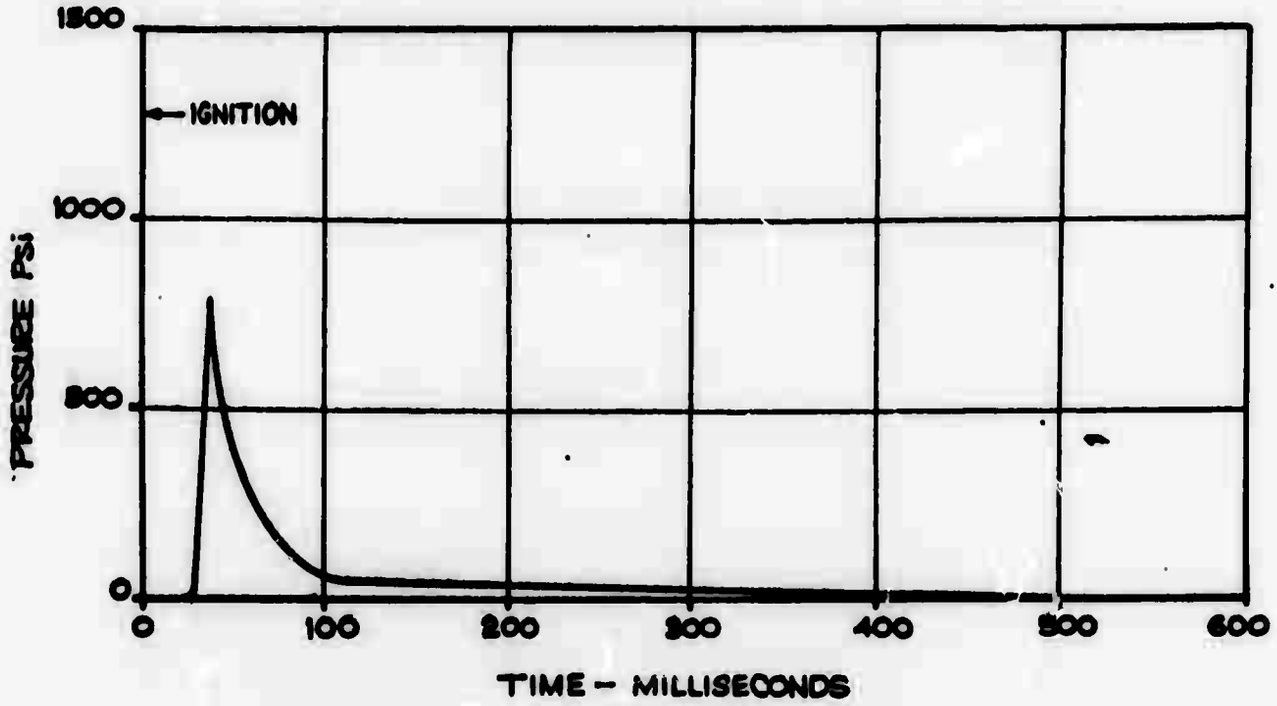


FIGURE 9 PRESSURE VS. TIME – TEST 6.25.70-1

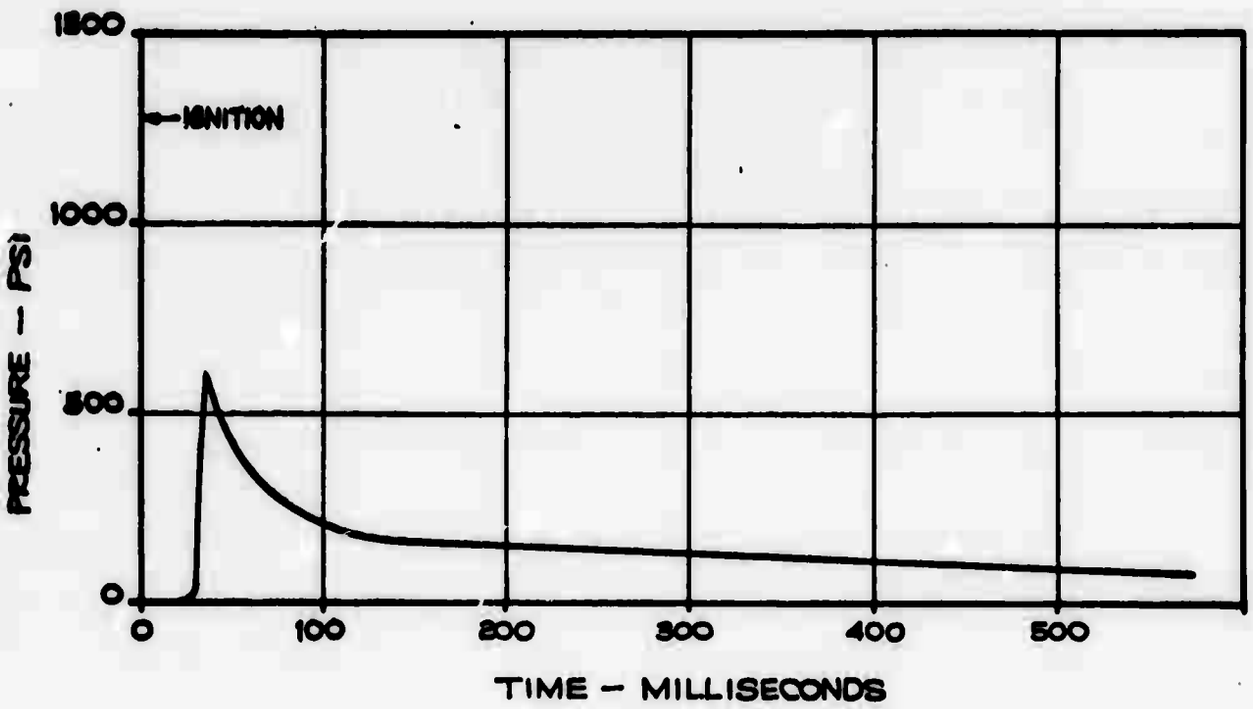


FIGURE 10 PRESSURE VS. TIME – TEST 7.21.70-1

A pressure trace for test 7.21.70-2 is given in Figure 11. The high peak pressure is indicative of a more energetic reaction resulting from the Be additive.

Residue analysis of solid material samples from this test gave weight fractions as shown in the table. The corresponding mole fractions are .66 Ba + .14 BaO + .06 BeO + .14 Be. Equilibrium calculations, made prior to the test assuming an ideal solution at 3000°K, gave predicted mole fractions of .71 Ba + .11 BaO + .09 BeO + .09 Be. The close agreement of these two sets of mole fractions indicates that something like an ideal equilibrium reaction does occur, at least before the mixture freezes. The competition for O_2 may terminate at or near the freezing point of BeO at 2703°K. This would explain the correlation with the 3000°K calculations.

In test 7.23.70-1, a venting test was done for reaction (2) with n = 3.2. In this test, the barium granules were pressed into the canister rather than loosely packed as in previous tests. The high pressure observed is due to the high temperature and decreased free volume. 55% of the chemical weight was vented in this test. Analysis of the residue was not made. As in test 6.24.70-1, a large, bright, homogenous fireball was observed.

In this test, as in all of the tests of reaction (2) or (3), considerable erosion of the exit orifice occurred and some melting of the steel inside the canister occurred. This evidence of high temperature has not been apparent in past tests of reaction (1). Figure 12 is a pressure trace for test 7.23.70.

Since some release of free Ba from BaO has been shown to occur in the presence of Be, test 8.20.70-1 was made to determine if Be would effectively release

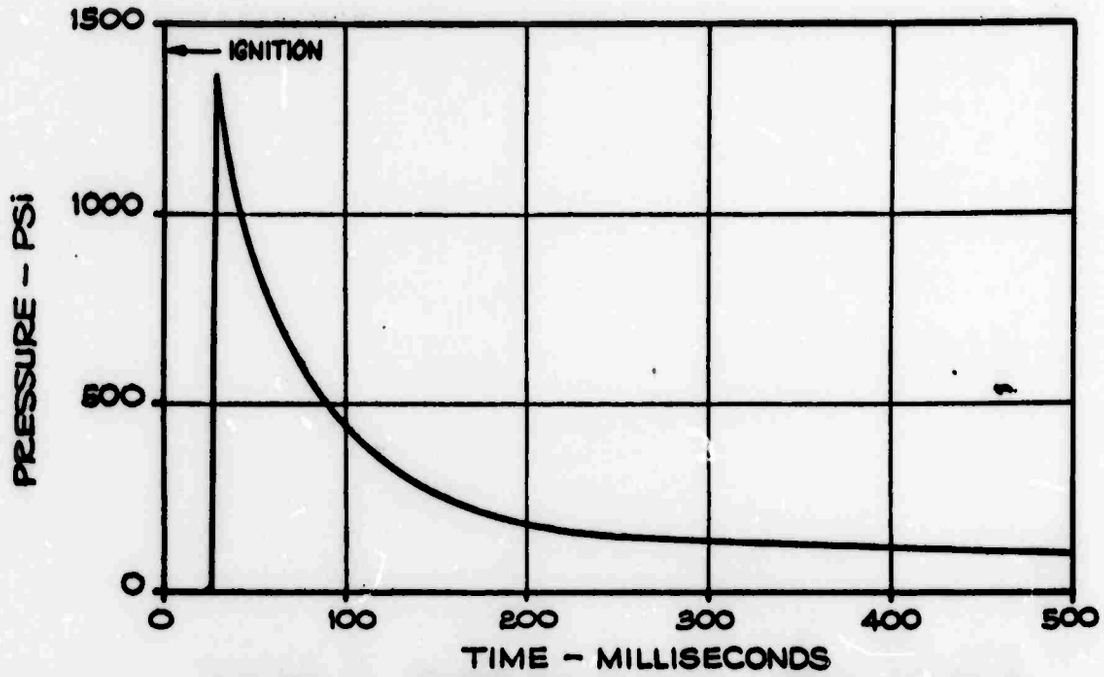


FIGURE 11 PRESSURE VS. TIME - TEST 7.21.70-2

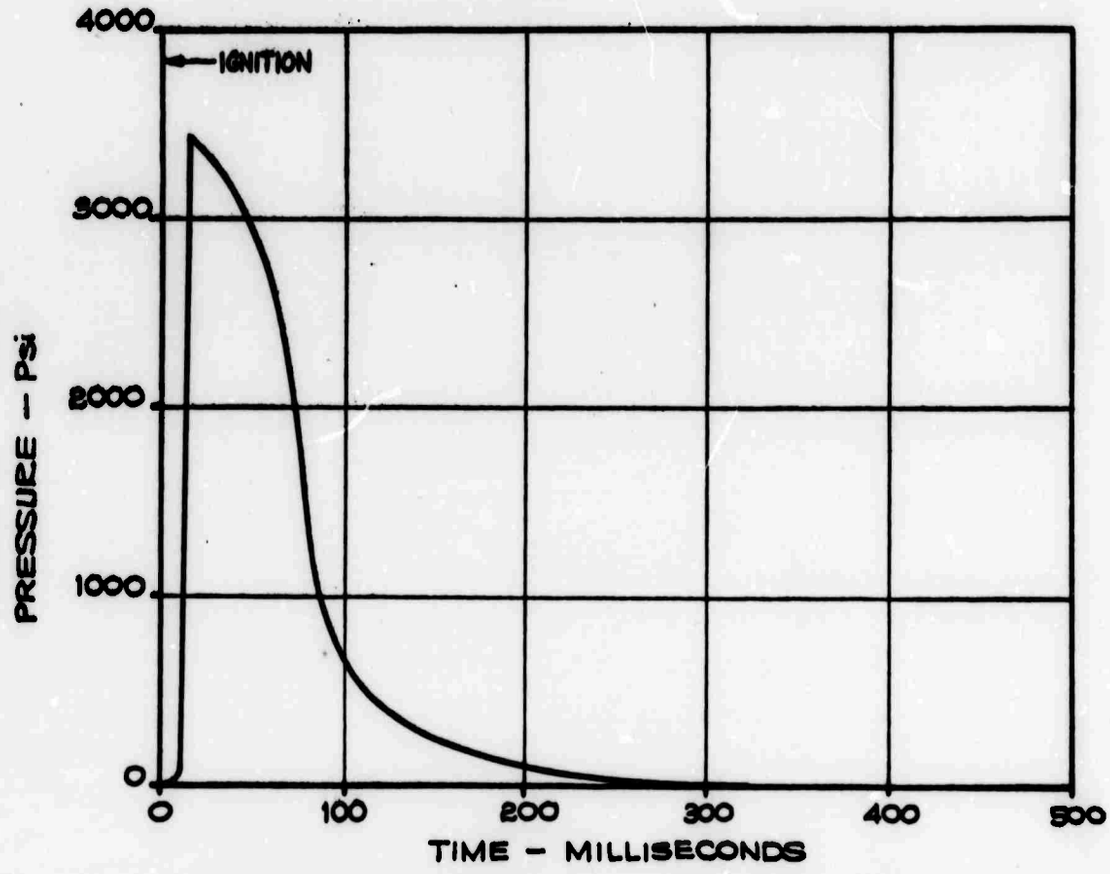


FIGURE 12 PRESSURE VS. TIME - TEST 7.23.70

-1277

free Ba from BaO_2. 748 grams of the two reactants were placed loose in a canister and ignited in the same manner that is typically used for reaction (1). A lower-than-expected peak pressure was observed, indicating that full reduction did not occur. Hydrogen evaluation analysis of the residue showed 45.6% Ba by weight in the products. Ideal equilibrium calculations at 3000°K predict 64% Ba. This reaction has potentially less yield than either (2) or (3) and lacks the safety advantage.

Tests 9.30.70-1 and 10.12.70-1 were made in preparation for the flight test "Tangerine." In the first of these tests a pressed charge of Ba was used as in test 7.23.70-1. Post-test observation of the opened can indicated that the O_2 did not fully mix with the pressed Ba and complete uniform combustion did not occur. For flight test purposes a one kilogram charge was chosen and tested in 10.12.70-1. In this test, complete O_2 mixing was apparent by observing a totally melted residue pool in the bottom of the canister.

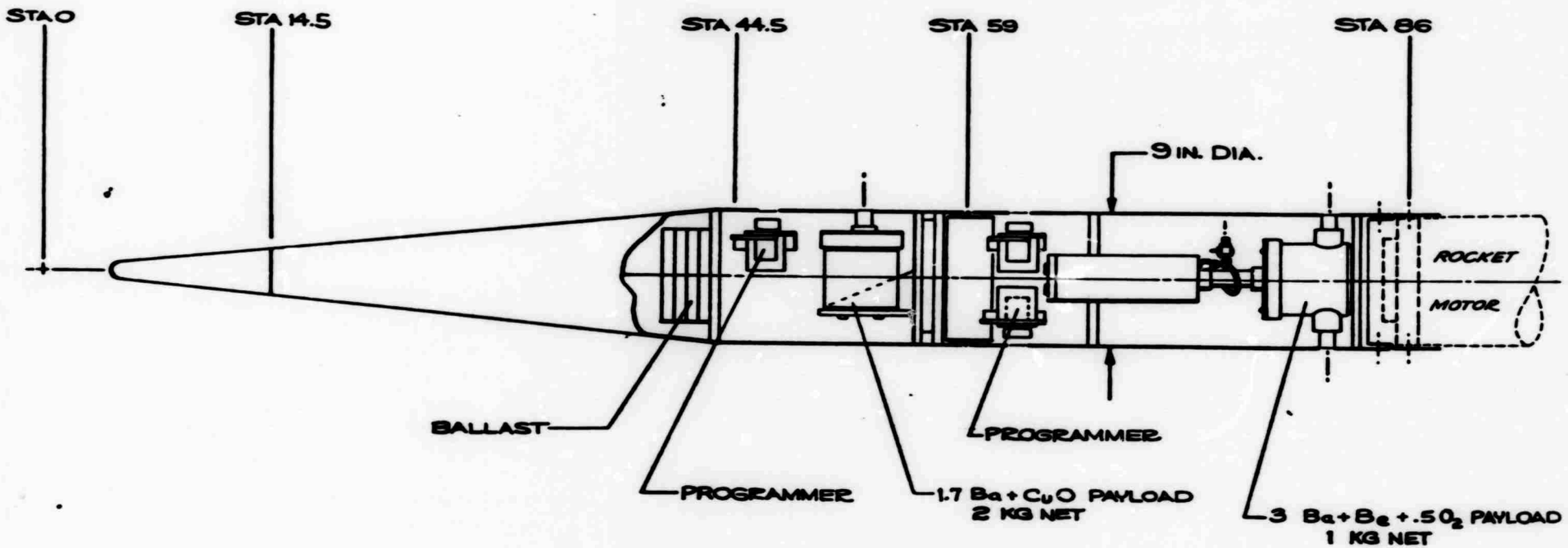
5. FLIGHT TEST - TANGERINE

A payload (Tangerine) consisting of a 2kg 1.7 Ba + CuO release as a control, and 1 kg 3 Ba + Be + .5 O_2 release carried aboard a Nike Hydac vehicle was successfully flight tested from Eglin in October 1970.

The test reactor illustrated in Figure 7 was used to carry the new chemistry The complete Tangerine payload is illustrated in Figure 13.

Table 4 is a summary of the Tangerine flight. HF observations for electron density were made by Raytheon Company, and optical observations for spectra and cloud motion were mode by Stanford Research Institute and Technology International Corporation.

The intent was that both releases would occur at 185 km but the trajectory was higher than planned and both payloads were released above 200 kilometers. As a result the peak electron densities were substantially lower than expected and direct backscatter from the clouds was not observed. The clouds were detected, however, via forward scatter paths invalving ionospheric reflections. The absence of direct backscatter echoes and the presence of forward scatter echoes has been used to place upper and lower bounds on the peak electron density in both clouds. It is concluded that the new mix produced a cloud having, at worst, the same peak electron density as that expected from the standard mix and, at best, 6 times as great[19].



GROSS WT. = 250 LB.

FIGURE 13 TANGERINE PAYLOAD

The minimum electron densities for these releases based on the Raytheon data were

Release	Ordinary	Extraordinary
Tangerine I (2 kg 1.7 Ba + CuO)	5.63×10^4 e/cm^3	5.62×10^4 e/cm^3
Tangerine II (1 kg^3 Ba + Be + 1/2 O_2)	1.64×10^5 e/cm^3	1.66×10^5 e/cm^3

TABLE 4 - FLIGHT TEST SUMMARY - TANGERINE

Launch Site: Eglin A-15

Launch Location: 30°23' 14.544" N Lat. 86°48' 13.286" W Long. Elevation 10.984 Ft.

Launch Date: 21 October 1970

Launch Time: 23 Hr. 40 Min. 59.410 Sec. ZULU

Vehicle:	Nike Hydac
Payload Gross Weight:	200 lb.
Launch Q.E.:	79°
Peak Altitude:	745 K-Ft.
Peak Range (Horizontal):	352 K-Ft.
Impact Range:	705 K-Ft.
Impact Azimuth:	161.3 Deg True

Tangerine I (1.7 Ba + CuO):

Chemical Weight	2015 gm
Barium Weight	1515 gm
Copper Oxide Weight	500 gm
Excess Barium Available	604 gm
Release Time	162 sec
Release Altitude	201 km
Release Range (Horizontal)	77.1 km

Tangerine II (3 Ba + Be + 1/2 O_2)

Chemical Weight	1060 gm
Barium Weight	1000 gm
Beryllium Weight	21 gm
Oxygen Weight	39 gm
Excess Barium Available	867 gm
Release Time	295 sec
Release Altitude	212.8 km
Release Range (Horizontal)	145.6 km

6. CONCLUSIONS AND RECOMMENDATIONS

Two new reaction systems using gaseous oxygen in a barium or barium-beryllium combustion reaction have been developed, and partially analyzed and tested.

It is estimated that an approximate 3.5 fold impravement over the standard 2.5 Ba + CuO system is now possible using either of these two reactions. A 95 kg gross weight payload carrying 48 kg of chemicals can now be designed to produce a likely yield of 16 kg of barium vapor. Additional flight tests are necessary to further substantiate these estimates and accomplishment of these is recommended during the completion of the program.

The benefits of the two-phase reactor system may, in the future, be extended to use the halogen gaseous and liquid oxidizers which have been temporarily set aside. Only minor changes in the reactor design should be necessary to accommodate any of these axidizers. The potential benefits of these have not been fully determined, but some improvement over the oxygen systems is possible. Further analysis is recommended together with determination of possible difficulties that might be introduced in the optical analysis of vapor clouds containing the halide products.

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